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(54) Synthetic resin composition and process for producing the same.

(57) A synthetic resin composition is provided which comprises at least one lanthanoid-containing compound selected from the group consisting of oxides, hydroxides, inorganic and/or organic acid salts and complexes of lanthanoids and a vinyl polymer.

The resin composition has a high neutron ray-shielding capacity and excellent optical and mechanical properties.

SYNTHETIC RESIN COMPOSITION AND PROCESS FOR PRODUCING THE SAME

The present invention relates to a synthetic resin composition having radiation-absorbtion properties and a process for producing the same.

Synthetic resins such as methacrylic resin have been used widely in various fields, since they have excellent transparency, weather resistance and mechanical properties. However, they could not be used for shielding radiation because they have no such properties.

Recently, radiation-shielding materials comprising a methacrylic resin containing lead have been developed (see Japanese Patent Publication No 2360/1960 and Japanese Patent Laid-Open Nos 9994/1978, 9995/1978, 9996/1978 and 63310/1978).

However, these radiation-shielding materials containing lead have only an insufficient capacity of shielding neutron rays, though they shield effectively electromagnetic waves such as X-rays and γ-rays and charged particles such as α-rays and β-rays.

It has been known to add a boron compound to a polyethylene or methacrylic resin to obtain a high-molecular material capable of shielding neutron rays (Japanese Patent Laid-Open No 144597/1980). According to this process, a high neutron rays-absorbing

capacity can be obtained. However, the capacity is gradually reduced as the neutron absorption proceeds, since helium and lithium formed by the neutron absorption have no appreciable neutron-absorbing capacity. Further, the optical and mechanical properties of the resin are yet unsatisfactory.

We have now found it possible to prepare synthetic resin compositions combining high neutron ray shielding capacity with good optical and chemical properties and of improved durability.

According to the present invention a synthetic resin composition is provided which contains a polymer comprising mainly a vinyl monomer and at least one compound containing a lanthanoid selected from the group consisting of oxides, hydroxides, inorganic and/or organic acid salts and complexes of lanthanoids.

The synthetic resin composition of the present invention can be obtained by incorporating a lanthanoid-containng compound into a synthetic resin.

Therefore, processes for obtaining the composition of the present invention are not particularly limited and various processes can be employed. For example, there may be mentioned a process wherein a lanthanoid-containing compound is blended with a synthetic resin, a process wherein a lanthanoid-containing compound is dispersed or dissolved in a resin-forming starting material selected from the group consisting of a vinyl monomer,

a mixture mainly comprising the vinyl monomer or a partial polymer thereof, and then polymerising the resin-forming starting material, or a process wherein a lanthanoid-containing compound is mixed with a vinyl monomer, a monomer mixture mainly comprising the vinyl monomer or a partial polymer thereof and a solvent to effect the polymerisation.

DETAILED DESCRIPTION OF THE INVENTION:

As the resin-forming starting material used for producing the resin composition of the present invention, there may be mentioned a vinyl monomer, for example, at least one monomer selected from the group consisting of acrylic acid, methacrylic acid or their esters, styrene and substituted styrene, a mixture thereof with another copolymerizable vinyl monomer and partial polymers of them.

In the present invention, methyl methacrylate is particularly preferred as the vinyl monomer from the viewpoint of its weather resistance, mechanical strength and transparency. As other monomers copolymerizable with the vinyl monomer, there may be mentioned compounds selected from the group consisting of alkyl acrylates containing 1 to 4 carbon atoms in the alkyl group, alkyl methacrylates containing 1 to 4 carbon atoms in the alkyl group, styrene, α-methylstyrene, cyclohexyl methacrylate, acrylonitrile, ethylene glycol dimethacrylate, ethylene glycol diacrylate, diethylene glycol dimethacrylate, diethylene glycol diacrylate, tetraethylene glycol dimethacrylate, tetraethylene glycol acrylate, pentaerythritol tetramethacrylate, pentaerythritol tetracrylate, allyl acrylate and allyl methacrylate. The monomer is used in an amount of up to 50 wt.% based on the monomer

mixture. The polymer content of the partial polymer used as the resin-forming starting material is desirably as low as possible for preventing damage to the high optical properties of the final polymer.

The lanthanoid-containing compound used for producing the composition of the present invention is at least one compound selected from the group consisting of oxides, hydroxides, inorganic and/or organic acid salts and complexes of a lanthanoid selected from the group consisting of lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutetium.

As the inorganic acid salts of the lanthanoids, there may be mentioned, for example, sulfates, nitrates, carbonates, phosphate and hydrochlorides. Among them, the nitrates are particularly preferred. They include, for example, those of gadolinium, samarium, europium, lanthanum, neodymium, cerium, praseodymium, erbium, thulium, ytterbium, lutetium, holmium, promethium, terbium and dysprosium as well as magnesium gadolinium nitrate (double salt).

As the organic acid salts of the lanthanoids, there may be mentioned, for example, acetate, octylate, propionate, butyrate, isobutyrate, caproate, caprylate, caprate, laurate, linoleate, linolenate, ricinoleate,

succinate, maleate, phthalate, naphthenate, levulinate, isovalerate, acetylvalerate, lactate, O-ethylglycolate, O-butylglycolate, butyl acid phosphate and ethyl acid phosphate.

As the organic acid salts, there may also be mentioned those of compounds of the general formula:

$$CH_2 = \overset{\displaystyle R}{\overset{|}{C}}\text{-COOH} \qquad (I)$$

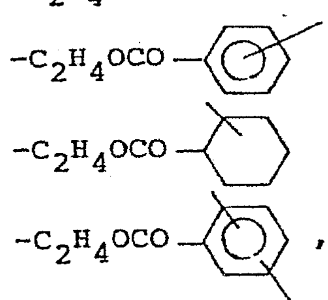
wherein R is a hydrogen atom or a methyl group, and those of compounds of the general formula:

$$CH_2 = \overset{\displaystyle R'}{\overset{|}{C}}\text{-COOR}''\text{-}(COOH)_n \qquad (II)$$

wherein R' is a hydrogen atom or a methyl group,

R" is $-C_2H_4OCOC_2H_4-$,

$-C_2H_4OCOCH{=}CH-$,



or

, and

n is 1 to 2.

As particular examples of the salts, there may be mentioned methacrylates, acrylates, 2-(meth)acryloxyethyl succinates, 2-(meth)acryloxyethyl maleates, 2-(meth)-acryloxyethyl phthalates, 2-(meth)acryloxyethyl

hexahydrophthalates and 2-(meth)acryloxyethyl trimellitates.

As the lanthanoid complex used in the present invention, there may be mentioned, for example, a complex obtained by reacting a lanthanoid chloride with a ß-diketone such as thenoyltrifluoroacetone, hexafluoroacetylacetone, pivaloyltrifluoroacetone, trifluoroacetylacetone, decafluoroheptanedione, heptafluorodimethyloctanedione, benzoyltrifluoroacetone, naphthoyltrifluoroacetone, dibenzoylmethane, benzoylacetone, acetylacetone, isonitrobenzoylacetone, 1-phenyl-2-methyl-4-benzoylpyrazolone-5 or isopropyltropolone, or cupferron.

The amount of the lanthanoid-containing compound is 0.001 to 10 wt.%, preferably 1 to 5 wt.%, (in terms of the lanthanoid atom) based on the resin composition. When this amount is less than 0.001 wt.%, the resulting resin composition exhibits only a poor neutron ray-shielding effect. When the amount exceeds 10 wt.%, the optical properties or mechanical strength of the composition is reduced.

The lanthanoid-containing compound may be incorporated into the synthetic resin by a method which varies depending on the use. For example, the compound is blended with the synthetic resin formed, or it is mixed with the resin-forming starting material

before polymerization or alternatively it is mixed with the resin-forming starting material and the solvent before polymerization. The last process wherein the solvent is used is preferred when a no light scattering, transparent resin product is intended.

In blending the compound with the synthetic resin or dispersing it in the resin-forming starting material, it is preferred to use, for example, an oxide, carbonate, hydroxide or complex of a lanthanoid having an average particle diameter of 0.2 to 20 μ. In mixing the compound with a mixture of the resin-forming starting material and the solvent, it is preferred to use an inorganic or organic acid salt such as nitrate, methacrylate or acrylate of a lanthanoid obtained by reacting a lanthanoid oxide with an inorganic or organic acid or a double salt thereof; or a complex compound such as tris(acetylacetonato)lanthanoid or tris(benzoylacetonato)lanthanoid obtained by reacting a lanthanoid chloride with acetylacetone or benzoylacetone.

As the solvent used in the polymerization reaction for forming the resin composition of the present invention, there may be mentioned a compound which can dissolve both the resin-forming starting material and the compound containing the lanthanoid, represented by the general formulae:

$$R_1-\overset{\overset{O}{\|}}{C}-OH \qquad (1)$$

wherein R_1 is a saturated or unsaturated hydrocarbon residue having 1 to 20 carbon atoms;

$$R_2-O-\overset{\overset{O}{\|}}{C}-R_3-\overset{\overset{O}{\|}}{C}-OH \qquad (2)$$

wherein R_2 is a saturated or unsaturated hydrocarbon residue having 1 to 9 carbon atoms and R_3 is a saturated or unsaturated hydrocarbon residue having 1 to 4 carbon atoms;

$$CH_2=\overset{\overset{R_4}{|}}{C}-\overset{\overset{O}{\|}}{C}-O-(A_1O)_n-H \qquad (3)$$

wherein R_4 is a hydrogen atom or a methyl group, A_1 is an alkylene group having 2 to 6 carbon atoms and n is an integer of 1 to 10;

$$CH_2=\overset{\overset{R_5}{|}}{C}-\overset{\overset{O}{\|}}{C}-O-R_6-OH \qquad (4)$$

wherein R_5 is a hydrogen atom or a methyl group and R_6 is an alkylene group having 2 to 6 carbon atoms;

$$R_7-OH \qquad (5)$$

wherein R_7 is a saturated or unsaturated hydrocarbon residue having 3 to 10 carbon atoms;

and

$$R_8 \leftarrow\!\!\!\!\left(A_2 - O\right)_m H \qquad (6)$$

Wherein R_8 is a hydroxyl group or a saturated or unsaturated hydrocarbon residue having 1 to 10 carbon atoms, A_2 is an alkylene group having 2 to 4 carbon atoms and m is an integer of 2 to 10.

Each of the solvent represented by the above general formula (1) through (6) is a cosolvent for homogeneously dissolving the lanthanoid-containing compound in the resin-forming starting material. As the solvents, there may be mentioned, for example, unsaturated carboxylic acids such as methacrylic acid and acrylic acid; saturated or unsaturated fatty acids such as propionic acid, octylic acid, isobutyric acid, hexanoic acid, octylbenzoic acid, stearic acid, palmitic acid and naphthenic acid; unsaturated alcohols such as 2-hydroxyethyl acrylate and 2-hydroxyethyl methacrylate; saturated aliphatic alcohols such as propyl alcohol and cyclohexyl alcohol; and glycols such as ethylene glycol, diethylene glycol and propylene glycol. Among these solvents, monomers copolymerizable with methyl methacrylate such as methacrylic acid, acrylic acid, 2-hydroxyethyl methacrylate and 2-hydroxyethyl acrylate, are preferred. These solvents may be used either alone or in the form of a combination of two or more of them. The amount of the solvent used in the present invention is various

depending on a variety and amount of the lanthanoid-containing compound. The amount is, however, up to 40 wt.%, preferably up to 10 wt.%. When it exceeds 40 wt.%, the mechanical and thermal properties of the resulting resin are unsatisfactory.

As a polymerization initiator used in the above-mentioned polymerization reaction, there may be mentioned known radical initiators such as a peroxide, e.g. benzoyl peroxide or lauroyl peroxide; and an azobis compound, e.g. 2,2'-azobisisobutyronitrile, 2,2'-azobis(2,4-dimethylvaleronitrile) or 2,2'-azobis(2,4-dimethyl-4-methoxyvaleronitrile). These polymerization initiators may be used either alone or in the form of a mixture of two or more of them. The amount of the initiator is 0.001 to 1.0 part by weight per 100 parts by weight of the starting material for resin.

Though the polymerization method for obtaining the resin composition of the present invention is not particularly limited, a casting polymerization is preferred. In this method, a mixture of the lanthanoid-containing compound, resin-forming starting material a solvent and optionally additives is poured into a mold constituted by, for example, inorganic glass plates, stainless steel plates, nickel-chromium plates or aluminum plates and a soft polyvinyl chloride gasket to effect the polymerization.

The casting polymerization is effected at 45 to 95°C for 0.3 to 15 hours and then at 100 to 145°C for 10 min. to 5 hours to complete the polymerization. The polymerization may be effected also by an ionizing radiation method at a low temperature.

The resin composition of the present invention may contain, if necessary, U.V. absorber, releasing agent, thermal stabilizer, colorant and light-scattering agent as well as another known neutron-shielding compound and lead compound.

When the lanthanoid-containing composition of the present invention having excellent optical and mechanical properties is used in combination with a lead compound, it becomes possible to shield all of X-rays, γ-rays and neutron rays. The resin composition of the invention is particularly useful as a thermal neutron, X-rays or γ-rays shielding material. The composition may be used also for the production of an optical filter, selective light absorption filter, illuminating filter, optical lens, optical converter, scintillator, light-emitting material, fluorescent substance-containing composition, refractive index modifier, colorant and illuminating material.

The following examples will further illustrate the present invention, which by no means limit the invention.

In the examples, the total transmission and haze were determined according to ASTM-D-1003-61. The bending breaking strength was determined according to ASTM-D-790. The thermal neutron absorption cross section was determined from values mentioned in "Jikken Kagaku Koza" (12) - Hosha Kagaku (published by Maruzen Co., Ltd.) and according to the following formula:

$$S = \left(\frac{W_1}{M_1} \times S_1 + \frac{W_2}{M_2} \times S_2 + \ldots + \frac{W_n}{M_n} \times S_n\right) \times N$$

wherein: S is a thermal neutron absorption cross section (cm^2) per 100g of the composition,

Mi is an atomic weight of the i-th element,

Wi is an amount of the i-th element,

Si is a thermal neutron absorption cross section of the i-th element (barns), and

N is an Avogadro number,

(i = 1 ..... n).

Referential Example 1

Synthesis of gadolinium methacrylate:

0.3g of hydroquinone monomethyl ether used as the polymerization inhibitor was homogeneously dissolved in a mixture of 280g of methacrylic acid and 1000g of toluene. The solution was heated to 60° C. 166g of powdery gadolinium oxide was added slowly to the solution

over 20 min and the resulting mixture was stirred for 1 hour.

The resulting reaction liquid was allowed to stand for one day and filtered. The filtrate was removed to obtain gadolinium methacrylate.
Yield: 357g.

Referential Example 2

Synthesis of gadolinium nitrate:

Slightly excess gadolinium oxide was dissolved in concentrated nitric acid under heating to effect the reaction. After 1 hour, the reaction liquid was filtered and the filtrate was cooled to precipitate crystalline gadolinium nitrate. Yield: 62%.

Referential Example 3

Synthesis of tris(acetylacetonato)gadolinium:

100cc of acetylacetone and 180g of gadolinium chloride were suspended in 3000cc of anhydrous diethyl ether and the resulting suspension was refluxed for 2 hours. Diethyl ether was distilled off to obtain crystalline tris(acetylacetonato)gadolinium. Yield: 65%.

Referential Example 4

Synthesis of samarium methacrylate:

0.3g of hydroquinone monomethyl ether as the polymerization inhibitor was homogeneously dissolved in a mixture of 280g of methacrylic acid and 1000g of

toluene. The solution was heated to 60°C. 174g of samarium oxide was added slowly to the solution over 20 min and the resulting mixture was stirred for 1 hour.

The resulting reaction liquid was allowed to stand for one day and filtered. The filtrate was removed to obtain samarium methacrylate. Yield: 370g.

Referential Example 5

Synthesis of samarium nitrate:

Slightly excess samarium oxide was dissolved in concentrated nitric acid under heating to effect the reaction. After 1 hour, the reaction liquid was filtered and the filtrate was cooled to precipitate crystalline samarium nitrate. Yield: 60%.

Referential Example 6

Synthesis of tris(acetylacetonato)samarium:

100cc of acetylacetone and 180g of samarium chloride were suspended in 3000cc of anhydrous diethyl ether and the resulting suspension was refluxed for 2 hours.Diethyl ether was distilled off to obtain crystalline tris(acetylacetonato)samarium. Yield: 65%.

Referential Example 7

Synthesis of europium methacrylate:

0.3g of hydroquinone monomethyl ether as the polymerization inhibitor was homogeneously dissolved in a mixture of 280g of methacrylic acid and 1000g of toluene.

The solution was heated to 60°C. 176g of powdery europium oxide was added slowly to the solution over 20 min and the resulting mixture was stirred for 1 hour.

The resulting reaction liquid was allowed to stand for one day and filtered. The filtrate was removed to obtain europium methacrylate. Yield: 350g.

Referential Example 8

Synthesis of europium nitrate:

Slightly excess europium oxide was dissolved in concentrated nitric acid under heating to effect the reaction. After 1 hour, the reaction liquid was filtered and the filtrate was cooled to precipitate crystalline europium nitrate. Yield: 65%.

Referential Example 9

Synthesis of tris(acetylacetonato)europium:

100cc of acetylacetone and 174g of europium chloride were suspended in 3000cc of anhydrous diethyl ether and the resulting suspension was refluxed for 2 hours. Diethyl ether was distilled off to obtain crystalline tris-(acetylacetonato)europium. Yield: 70%.

Example 1

3g of gadolinium nitrate synthesized in Referential Example 2 was dissolved in a mixture of 17g of 2-hydroxyethyl methacrylate and 2g of propylene glycol. 78g of methyl methacrylate was added to the solution and they

were stirred to obtain a transparent liquid mixture.

0.04g of 2,2'-azobis(2,4-dimethylvaloronitrile) as the polymerization catalyst and 0.005g of sodium dioctyl sulfosuccinate as the releasing agent were dissolved in the liquid mixture. After degasification, the solution was poured into an ordinary inorganic glass mold designed for forming a plate of 3 mm thickness. The mold was immersed in warm water at 65°C for 180 min and then kept in an air bath at 110°C for 120 min to complete the polymerization. A resin plate taken out of the mold was transparent.

Example 2

1.5g of gadolinium nitrate synthesized in Referential Example 2 was dissolved in 8.5g of 2-hydroxyethyl methacrylate. The resulting solution was added to 90g of methyl methacrylate and they were stirred to obtain a transparent liquid mixture. The same polymerization catalyst and releasing agent in the same amounts as in Example 1 were added to the liquid mixture and the casting polymerization was carried out under the same conditions as in Example 1. The resulting resin plate was transparent.

Example 3

1.5g of tris(acetylacetonato)gadolinium synthesized in Referential Example 3 was dissolved in 8.5g of methacrylic acid. The resulting solution was added

to 90g of methyl methacrylate and they were stirred.

The same polymerization catalyst and releasing agent in the same amounts as in Example 1 were added to the liquid mixture and the casting polymerization was carried out in the same manner as in Example 1. A resin plate taken out of the mold after completion of the polymerization was transparent.

Example 4

8g of gadolinium methacrylate synthesized in Referential Example 1 was mixed with 2g of n-octylic acid, 1g of propylene glycol, 1g of 2-hydroxyethyl methacrylate, 5g of styrene and 83g of methyl methacrylate. The casting polymerization was effected under the same polymerization conditions as in Example 1. The resulting resin plate was transparent.

Example 5

3g of gadolinium acrylate, 3g of samarium methacrylate, 1g of europium methacrylate, 3g of n-octylic acid, 1g of propylene glycol and 89g of methyl methacrylate were mixed together. The casting polymerization was carried out under the same polymerization conditions as in Example 1. The resulting resin plate was transparent.

Example 6

4g of gadolinium methacrylate obtained in Referential Example 1, 4g of lead methacrylate, 3g of n-octylic acid,

2g of propylene glycol, 1g of 2-hydroxyethyl methacrylate and 86g of methyl methacrylate were mixed together. The casting polymerization was carried out under the same conditions as in Example 1. The resulting resin plate was transparent.

Example 7

0.04 part by weight of α,α'-azobis(2,4-dimethylvaleronitrile) as the polymerization catalyst, 0.005 part by weight of sodium dioctyl sulfosuccinate as the releasing agent and 2.0 parts by weight of gadolinium oxide having an average particle diameter of 2 μ were added to 100 parts by weight of a partial polymer (polymer content : 18%) of methyl methacrylate. They were stirred, degasified and poured into a mold for forming a plate of 3 mm thickness which mold was constituted by a reinforced glass and a soft vinyl chloride gasket. The mold was immersed in warm water at 70°C for 60 min and then kept in an air bath at 130°C for 80 min to complete the polymerization, thereby obtaining a resin plate.

Example 8

2.0 parts by weight of gadolinium hydroxide having an average particle diameter of 0.5 μ and 1.0 part by weight of gadolinium carbonate having an average particle diameter of 2 μ were added to 100 parts by

weight of a methacrylic resin (Acrypet VH; a trade mark of Mitsubishi Rayon Co., Ltd.). They were mixed thoroughly with a tumbler to obtain a homogeneous mixture. The mixture was extruded through an extruder by an ordinary method to obtain a sheet having 3 mm thickness.

Example 9

3g of samarium nitrate synthesized in Referential Example 5 was dissolved in a liquid mixture of 17g of 2-hydroxyethyl methacrylate and 2g of propylene glycol. 78g of methyl methacrylate was added to the solution and they were stirred to obtain a transparent liquid.

Then, the same polymerization catalyst and releasing agent in the same amounts as in Example 1 were added to the liquid mixture and the casting polymerization was carried out in the same manner as in Example 1. A resin plate taken out of the mold was transparent.

Example 10

1.5g of samarium nitrate synthesized in Referential Example 5 was dissolved in 8.5g of 2-hydroxyethyl methacrylate. The resulting solution was added to 90g of methyl methacrylate and they were stirred to obtain a transparent liquid mixture. The same polymerization

catalyst and releasing agent in the same amounts as in Example 1 were added to the liquid mixture and the casting polymerization was carried out in the same manner as in Example 1 to obtain a transparent resin plate.

Example 11

1.5g of tris(acetylacetonato)samarium synthesized in Referential Example 6 was dissolved in 8.5g of methacrylic acid. The resluting solution was added to 90g of methyl methacrylate and they were stirred.

The same polymerization catalyst and releasing agent in the same amounts as in Example 1 were added to the liquid mixture and the casting polymerization was carried out in the same manner as in Example 1. A resin plate taken out of the mold after completion of the polymerization was faintly yellow and transparent.

Example 12

8g of samarium methacrylate synthesized in Referential Example 4, 2g of n-octylic acid, 1g of propylene glycol, 1g of 2-hydroxyethyl methacrylate, 5g of styrene and 83g of methyl methacrylate were mixed together. The casting polymerization was effected under the same polymerization conditions as in Example 1. The resulting resin plate was faintly yellow and transparent.

Example 13

The same procedure as in Example 7 was repeated except that 2.0 parts by weight of gadolinium oxide was replaced with 2.0 parts by weight of samarium oxide.

Example 14

The same procedure as in Example 8 was repeated except that 2.0 parts by weight of gadolinium hydroxide and 1.0 part by weight of gadolinium carbonate were replaced with 2.0 parts by weight of samarium hydroxide and 1.0 part by weight of samarium carbonate.

Example 15

The same procedure as in Example 1 was repeated except that 3g of gadolinium nitrate was replaced with 3g of europium nitrate synthesized in Referential Example 8. A resin plate taken out of the mold was transparent.

Example 16

The same procedure as in Example 2 was repeated except that 1.5g of gadolinium nitrate was replaced with 1.5g of europium nitrate. The resulting resin plate was transparent.

Example 17

The same procedure as in Example 3 was repeated except that 1.5g of tris(acetylacetonato)gadolinium was

replaced with 1.5g of tris(acetylacetonato)europium synthesized in Referential Example 9. A resin plate taken out of the mold after completion of the polymerization was transparent.

Example 18

The same procedure as in Example 4 was repeated except that 8g of gadolinium methacrylate was replaced with 8g of europium methacrylate synthesized in Referential Example 7. The resulting resin plate was transparent.

Example 19

The same procedure as in Example 7 was repeated except that 2.0 parts by weight of gadolinium oxide was replaced with 2.0 parts by weight of europium oxide.

Example 20

The same procedure as in Example 8 was repeated except that gadolinium hydroxide and gadolinium carbonate were replaced with europium hydroxide and europium carbonate, respectively.

The results of the examination of the total transmission (%), haze (%), bending breaking strength (kg/cm^2) and neutron-shielding capacity (thermal neutron absorption cross section) of the methacrylic resin plates obtained in Examples 1 to 20 are shown in Table 1.

Table 1

	Total trans-mission (%)	Haze (%)	Bending breaking strength (kg/cm^2)	Thermal neutron absorption cross section (cm^2)
Ex. 1	92.2	1.5	740	2400
" 2	92.4	1.8	750	1200
" 3	92.5	1.8	720	840
" 4	91.2	2.0	700	5400
" 5	92.2	1.5	650	2700
" 6	90.3	2.7	680	2700
" 7	90.5	80	680	3400
" 8	89.5	85	675	5200
" 9	92.1	1.5	735	300
" 10	92.1	1.7	740	150
" 11	92.0	2.0	700	100
" 12	91.0	2.5	700	670
" 13	89.5	78	675	430
" 14	88.2	87	680	550
" 15	92.3	1.6	720	250
" 16	92.1	1.6	720	125
" 17	92.4	2.0	720	87
" 18	91.0	1.8	680	550
" 19	90:2	75	675	360
" 20	89.0	82	675	660
Ref. Ex. methacrylic resin plate (registered trademark: Shinkolyte S; a product of Mitsubishi Rayon Co., Ltd.)	93.0	.1	1200	up to 2

Examples 21 to 25 and Comparative Examples 1 and 2

Resin plates were prepared in the same manner as in Example 1 except that the concentration of gadolinium nitrate synthesized in Referential Example 2 was altered as shown in Table 2. Their physical properties are also shown in Table 2.

Table 2

	Gadolinium nitrate					
	Amount (g)	Atomic conc. of gadolinium in the total composition (%)	Total trans-mission (%)	Haze (%)	Bending bleaking strength (kg/cm^2)	Thermal neutron absorption cross section (cm^2)
Comp. Ex. 1	0	0	93	1	1200	up to 2
Ex. 21	0.022	0.01	92	1	1100	20
Ex. 22	0.22	0.1	92	1	1100	180
Ex. 23	1.1	0.5	92	1	820	880
Ex. 24	2.2	1.0	92	1	700	1800
Ex. 25	11.0	5.0	90	8	700	8800
Comp. Ex. 2	33.0	15.0	75	82	120	26000

Example 26

3g of neodymium nitrate produced in the same manner as in Referential Example 2 was dissolved in 8.5g of 2-hydroxyethyl methacrylate.88.5g of styrene was

added to the resulting solution and they were stirred. 0.05 g of 2,2'-azobis(2,4-dimethylvaleronitrile) as the polymerization catalyst and 0.005g of sodium dioctyl sulfosuccinate as the releasing agent were dissolved in the liquid mixture. After degasification, the mixture was poured in an ordinary inorganic glass mold designed for forming a plate of 3 mm thickness. The mold was immersed in warm water at 65°C for 180 min and then kept in an air bath at 110°C for 120 min to complete the polymerization. Thus, a transparent resin plate was obtained.

Example 27

The same procedure as in Example 2 was repeated except that methyl methacrylate was replaced with styrene. The resulting resin was transparent.

Example 28

The same procedure as in Example 3 was repeated except that tris(acetylacetonato)gadolinium was replaced with tris(acetylacetonato)neodymium and methyl methacrylate was replaced with styrene. The resulting resin plate was transparent.

Example 29

2.0 parts by weight of neodymium hydroxide having an average particle diameter of 0.5 μ and 1.0 part by weight of neodymium carbonate having an average particle

diameter of 2 µ were added to 100 parts by weight of AS resin (trade name: Lytak #330; a product of Mitsui Toatsu Chemicals, Inc.). They were mixed thoroughly by means of a tumbler and then extruded through an extruder by an ordinary method to obtain a sheet having 3 mm thickness.

Example 30

4 g of gadolinium 2-(meth)acryloxyethyl succinate, 2 g of n-octylic acid, 1 g of propylene glycol, 1 g of 2-hydroxyethyl methacrylate and 92g of methyl methacrylate were mixed together. The casting polymerization was carried out under the same polymerization conditions as in Example 1. The resulting resin plate was transparent and had physical properties equivalent to those of the resin obtained in Example 1.

Example 31

The casting polymerization was carried out in the same manner as in Example 1 except that gadolinium nitrate was replaced with erbium nitrate, lanthanum nitrate, praseodymium nitrate or ytterbium nitrate. The resulting resin plates were transparent.

CLAIMS

1. A synthetic resin composition comprising at least one lanthanon compound selected from oxides, hydroxides, inorganic and/or organic acid salts and complexes, and a polymer comprising from 50 to 100% of vinyl polymer units.

2. A resin composition according to claim 1 wherein the polymer is a homopolymer or a copolymer obtained by polymerising at least one monomer selected from acrylic acid, methacrylic acid and esters thereof or a copolymer obtained by polymerising a monomer mixture of the above-mentioned monomers with another copolymerisable ethylenic monomer.

3. A resin composition according to claim 1 wherein the polymer is a styrene homopolymer or copolymer.

4. A resin composition according to claim 3 wherein the lanthanon is neodymium.

5. A resin composition according to any preceding claim wherein the lanthanon compound is a sulfate, nitrate, carbonate, phosphate or hydrochloride.

6. A resin composition according to any of claims 1 to 4 wherein the lanthanon compound is an acetate, octylate, caproate, caprylate, laurate, isoburyrate or isovalerate or a double salt thereof.

7. A synthetic resin composition according to any of claims 1 to 4 wherein the lanthanon compound is a salt of an organic acid of the general formula

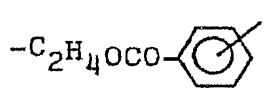
$$CH_2 = \overset{\displaystyle R}{\overset{|}{C}} - COOH \qquad (I)$$

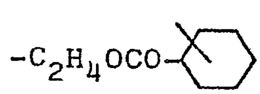
wherein R is a hydrogen atom or a methyl group, or of the general formula:

$$CH_2 = \overset{\displaystyle R'}{\overset{|}{C}} - COOR'' \text{——} (COOH)_n \qquad (II)$$

wherein R' is a hydrogen atom or a methyl group, R" is $-C_2H_4OCOC_2H_4-$

$-C_2H_4OCOCH{=}CH'-$





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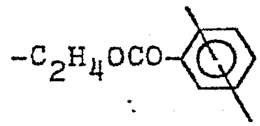
, and

$\underline{n}$ is 1 to 2.

8. A synthetic resin composition according to any of claims 1 to 4 wherein the complex of lanthanon compound is a complex obtained by reacting a lanthanon compound with a β-diketone or cupferron.

9. A synthetic resin composition according to any preceding claim wherein the concentration of the lanthanon compound is 0.001 to 10 wt.% based on the total composition.

10. A process for producing a synthetic resin composition according to any one of the preceding claims which comprises dispersing or dissolving at least one said lanthanon compound in a resin-forming starting material selected from vinyl monomers, monomer mixtures mainly comprising a vinyl monomer and partial polymers thereof and then polymerising the resin-forming starting material.

11. A process according to claim 10 wherein the vinyl monomer comprises at least one member of the group selected from methacrylic acid, acrylic acid and esters thereof.

12. A process according to claim 10 wherein the vinyl monomer is styrene or a monomer mixture mainly comprising styrene.

13. A process according to claim 10, 11 or 12 wherein the polymerisation is effected in a solvent capable of dissolving both the starting material and the lanthanon compound.

14. A process according to claim 13 wherein the solvent is represented by one of the following formulae:

$$R_1-\overset{\overset{\displaystyle O}{\|}}{C}-OH \quad (1)$$

wherein R_1 is a saturated or unsaturated hydrocarbon residue having 1 to 20 carbon atoms;

$$R_2-O-\overset{\overset{\displaystyle O}{\|}}{C}-R_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH \qquad (2)$$

wherein R_2 is a hydrogen atom or a saturated or unsaturated hydrocarbon residue having 1 to 9 carbon atoms and R_3 is a saturated or unsaturated hydrocarbon residue having 1 to 4 carbon atoms;

$$CH_2 = \overset{\overset{\displaystyle R_4}{|}}{C}-\overset{\overset{\displaystyle O}{\|}}{C}-O-\!\!-(A_1O)_n-\!\!-H \qquad (3)$$

wherein R_4 is a hydrogen atom or a methyl group, A_1 is an alkylene group having 2 to 6 carbon atoms and is an integer of 1 to 10;

$$CH_2 = \overset{\overset{\displaystyle R_5}{|}}{C} - \overset{\overset{\displaystyle O}{\|}}{C} - O - R_6 - OH \qquad (4)$$

wherein R_5 is a hydrogen atom or a methyl group and R_6 is an alkylene group having 2 to 6 carbon atoms;

$$R_7-OH \qquad (5)$$

wherein R_7 is a saturated or unsaturated hydrocarbon residue having 3 to 10 carbon atoms; and

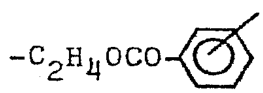
$$R_8 \text{---} (A_2-O)_m \text{---} H \qquad (6)$$

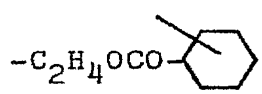
wherein R_8 is a hydroxyl group or a saturated or unsaturated hydrocarbon residue having 1 to 10 carbon atoms, A_2 is an alkylene group having 2 to 4 carbon atoms and <u>m</u> is an integer of 2 to 10.

15. A process according to claim 13 or 14 wherein the solvent is selected from unsaturated carboxylic acids, saturated or unsaturated fatty acids, esters containing a hydroxyl group, unsaturated or saturated alcohols and glycols.

16. A process according to any of claims 1 to 15 wherein the amount of the solvent added is up to 40 wt.%.

17. A process for producing a synthetic resin composition according to any of claims 1 to 9 which comprises blending at least one said lanthanon compound with a said polymer.


$-C_2H_4OCO-$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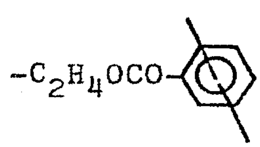
$-C_2H_4OCO-$

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(54) Synthetic resin composition and process for producing the same.

(57) A synthetic resin composition is provided which comprises at least one lanthanoid-containing compound selected from the group consisting of oxides, hydroxides, inorganic and/or organic acid salts and complexes of lanthanoids and a vinyl polymer.

The resin composition has a high neutron ray-shielding capacity and excellent optical mechanical properties.

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EUROPEAN SEARCH REPORT

Application number

EP 83 30 6711

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
X	DE-B-1 297 869 (CHEMISCHE WERKE HÜLS AG) * Claim; column 2, lines 2-4 * ---	1,3,9,17	C 08 K 3/10 C 08 K 5/00 C 08 F 2/44 C 08 L 25/04 C 08 L 33/00 // G 21 F 1/10
A	US-A-3 950 271 (R. LINARES et al.) * Claims * -----	1,17	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 3)
			C 08 K C 08 L G 21 F

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	13-02-1984	HOFFMANN K.W.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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